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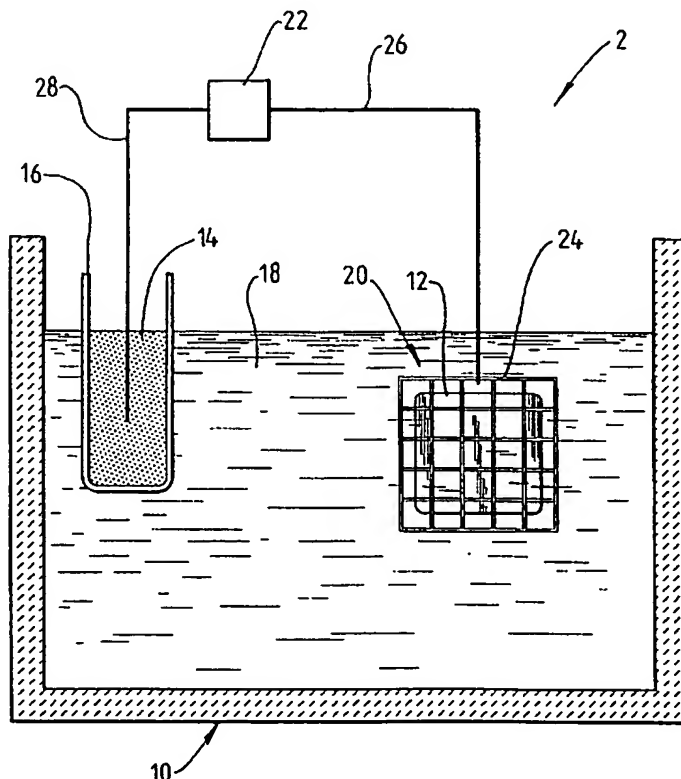
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(54) Title: ELECTROCHEMICAL REDUCTION OF METAL OXIDES



(57) Abstract: An electrochemical cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, is disclosed. The cell includes (a) a molten electrolyte (18), (b) a cathode (20) formed at least in part from the metal oxide in contact with the electrolyte, (c) an anode (14), and (d) a membrane (16) that separates the electrolyte and the anode. The membrane is permeable to oxygen cations and is impermeable to dissolved metal in the electrolyte. Optionally, the membrane is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms. An electrochemical method based on the above cell is also disclosed.

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## ELECTROCHEMICAL REDUCTION OF METAL OXIDES

The present invention relates to electrochemical reduction of metal oxides.

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The present invention was made during the course of an on-going research project on electrochemical reduction of metal oxides being carried out by the applicant. The research project has focussed on the reduction of titania ( $\text{TiO}_2$ ).

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During the course of the research project the applicant carried out experimental work on the reduction of titania using electrolytic cells that included a pool of molten  $\text{CaCl}_2$ -based electrolyte, an anode formed from graphite, and a range of cathodes.

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The  $\text{CaCl}_2$ -based electrolyte was a commercially available source of  $\text{CaCl}_2$ , namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of  $\text{CaO}$ .

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The applicant operated the electrolytic cells at potentials above the decomposition potential of  $\text{CaO}$  and below the decomposition potential of  $\text{CaCl}_2$ .

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The applicant found that at these potentials the cells could electrochemically reduce titania to titanium with low concentrations of oxygen, ie concentrations less than 0.2 wt %.

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The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage.

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Nevertheless, whilst not wishing to be bound by the comments in the following paragraphs, the applicant offers the following comments by way of an outline of a

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possible cell mechanism.

The experimental work carried out by the applicant produced evidence of Ca metal dissolved in the electrolyte. The applicant believes that the Ca metal was the result of electrodeposition of  $\text{Ca}^{++}$  cations as Ca metal on the cathode.

As is indicated above, the experimental work was carried out using a  $\text{CaCl}_2$ -based electrolyte at a cell potential below the decomposition potential of  $\text{CaCl}_2$ . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of  $\text{Ca}^{++}$  cations and  $\text{O}^{--}$  anions derived from CaO in the electrolyte. The decomposition potential of CaO is less than the decomposition potential of  $\text{CaCl}_2$ . In this cell mechanism the cell operation is dependent on decomposition of CaO, with  $\text{Ca}^{++}$  cations migrating to the cathode and depositing as Ca metal and  $\text{O}^{--}$  anions migrating to the anode and forming CO and/or  $\text{CO}_2$  (in a situation in which the anode is a graphite anode) and releasing electrons that facilitate electrolytic deposition of Ca metal on the cathode.

The applicant believes that the Ca metal that deposits on the cathode participates in chemical reduction of titania resulting in the release of  $\text{O}^{--}$  anions from the titania.

The applicant also believes that the  $\text{O}^{--}$  anions, once extracted from the titania, migrate to the anode and react with anode carbon and produce CO and/or  $\text{CO}_2$  (and in some instances CaO) and release electrons that facilitate electrolytic deposition of Ca metal on the cathode.

However, notwithstanding that the cell could electrochemically reduce titania to titanium with very low

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concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon transferred from the anode to the electrolyte and to the titanium produced at the cathode under a wide range of cell operating conditions. Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was responsible for low current efficiency of the cell. Both problems are significant barriers to commercialisation of the electrochemical reduction technology.

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The applicant carried out experimental work to identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

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In the course of the experimental work the applicant made the invention that is described and claimed in International application PCT/AU02/00457 in the name of the applicant. The invention minimises carbon contamination by replacing the carbon anode with a molten metal anode.

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In broad terms, the invention that is described and claimed in the International application provides an electrolytic cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode formed at least in part from the metal oxide in contact with the electrolyte, and (c) a molten metal anode in contact with the electrolyte.

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In addition, in broad terms the invention that is described and claimed in the International application is a method of electrochemically reducing a metal oxide, such as titania, in a solid state in an electrolytic cell, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode

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being formed at least in part from the metal oxide, and  
(c) a molten metal anode in contact with the electrolyte,  
and which method includes applying a cell potential across  
the anode.

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The present invention is an improvement of the  
invention described and claimed in the International  
application.

10

According to the invention there is provided an  
electrochemical cell for electrochemical reduction of a  
metal oxide, such as titania, in a solid state, which  
electrochemical cell includes (a) a molten electrolyte,  
(b) a cathode formed at least in part from the metal oxide  
15 in contact with the electrolyte, (c) an anode, and (d) a  
membrane that separates the electrolyte and the anode and  
is permeable to oxygen cations and is impermeable to  
dissolved metal in the electrolyte, and optionally is  
impermeable to any one or more of (i) electrolyte anions  
20 other than oxygen anions, (ii) anode metal cations, and  
(iii) any other ions and atoms.

The above-described membrane prevents back  
reaction of dissolved metal in the electrolyte and oxygen  
25 atoms generated at the anode that can significantly reduce  
the current efficiency of the cell. Specifically, the  
membrane allows oxygen anions to migrate to the anode and  
give up electrons at the anode and prevents dissolved  
metal in the electrolyte migrating to the anode and  
30 reacting with oxygen atoms generated at the anode.

Accordingly, the membrane makes it possible for  
the cell to operate at high current efficiencies.

35

In a situation in which the membrane is also  
impermeable to electrolyte anions other than oxygen  
anions, the membrane makes it possible to operate the cell

- 5 -

at higher potentials without the disadvantages that are often associated with operating at such higher cell potentials. For example, in situations in which the electrolyte includes  $\text{CaCl}_2$ , it is undesirable to operate at potentials that result in evolution of chlorine gas because of the corrosive and toxic properties of the gas. The membrane prevents the migration of  $\text{Cl}^-$  anions to the anode and thereby prevents the evolution of chlorine gas. Operating at higher cell potentials is advantageous because it produces higher currents and therefore reduces cycle times.

In a situation in which the membrane is also impermeable to anode metal cations it is possible to use anode materials that would react with the electrolyte save for the membrane separating the anode and the electrolyte. Thus, there is a wider selection of anode materials that are available.

Preferably the anode is a molten metal anode.

However, the present invention also extends to other arrangements. For example, the present invention extends to fuel cell arrangements in which there is (a) a coating of a suitable metal/metal oxide system, such as  $\text{Ni/NiO}$ , on the membrane that forms the anode and conducts electrons released by the oxygen anions and (b) a fuel, such as hydrogen or natural gas, that consumes oxygen that is evolved at the anode.

The anode may be arranged so that oxygen gas is evolved at the anode and is removed from the cell.

The anode may be also be arranged so that there is no oxygen gas released from the anode assembly. Specifically, the anode may include a means for scavenging oxygen that is generated at the anode when oxygen anions

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migrate to the anode and give up electrons at the anode. The above-described gaseous fuel is one suitable scavenging means. The scavenging means may also be a solid material that is oxidised by oxygen.

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The use of solid scavenging materials is preferred in situations in which the anode is a molten metal anode. Suitable solid scavenging materials for molten silver anodes include iron, carbon and tungsten.

10 The use of a scavenging means reduces the need to select molten metal anodes that have high solubility of oxygen in anode metal.

Preferably the solid scavenging materials form  
15 the anode electrode for molten metal anodes.

It is preferred that the membrane be impermeable to the anode electrode material.

20 The present invention is based on experimental work carried out by the applicant to electrochemically reduce titania.

The experimental work was carried out on a cell  
25 that included a stainless steel crucible containing molten  $\text{CaCl}_2$ -based electrolyte containing at least some  $\text{CaO}$ , a cathode extending into the electrolyte, the cathode including  $\text{TiO}_2$ , and an anode in the form of molten silver contained in a yttria stabilised zirconia crucible  
30 extending into the electrolyte.

The yttria stabilised zirconia is permeable to oxygen anions and is impermeable to calcium metal dissolved in the electrolyte, chlorine anions, and silver  
35 cations.

The anode electrical connection was made via a



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low carbon steel wire extending into the molten silver.  
The cell was operated initially at a potential around 3V.

5 It was found that oxygen was removed from the  
cell - by oxidation of the steel electrode - under these  
conditions at high current efficiencies. Operation at  
high current efficiencies indicated that there was no back  
reaction of calcium metal and oxygen generated at the  
anode.

10

The cell was also operated at higher potentials,  
up to 10V. It was found that there was decomposition of  
 $\text{CaCl}_2$  and no evolution of chlorine gas under these  
conditions. There was also a proportional increase in  
15 current with increasing voltage.

The experimental work opens up the following  
possibilities for an electrolytic cell for  
electrochemically reducing metal oxides, such as titania.

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- Operating the cell at high current efficiencies - with  
minimal back reaction.
- Operating the cell at high voltages resulting in high  
25 currents, and thereby reducing cycle time.
- Operating the cell with an oxygen scavenger in the  
anode assembly, thereby eliminating difficulties with  
handling oxygen gas at high temperatures. Scavengers  
30 for molten silver anodes include iron, carbon, and  
tungsten.
- Alternatively, operating the cell with an anode that  
generates oxygen gas and removing oxygen gas from the  
35 anode assembly.

In a situation in which the anode is a molten

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metal anode, preferably the metal is chosen such that its melting point is within the operating temperature range of the electrolyte.

5                    Preferably the melting point of the metal of the molten metal anode is higher than the melting point of the electrolyte and lower than the vaporisation and/or decomposition temperature of the electrolyte in order to prevent electrolyte consumption and removal through  
10 vaporisation.

                  Preferably the metal of the molten metal anode is silver or copper.

15                   Preferably the membrane is formed from a solid electrolyte.

                  Preferably the solid electrolyte is an oxide.

20                   More preferably the solid electrolyte is yttria stabilised zirconia.

                  Preferably the membrane includes a body and an outer lining, with the outer lining being in contact with  
25 the electrolyte, and the outer lining being formed from a material that is inert with respect to dissolved metal in the electrolyte and is impermeable to the dissolved metal.

                  In a situation in which the metal oxide is  
30 titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents. In this situation calcium metal will be the dissolved metal in the electrolyte.

35                   Preferably the body is formed from the solid electrolyte.

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Preferably the outer lining is formed from a rare earth oxide.

More preferably the rare earth oxide is yttria.

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Preferably the lining is continuous and covers all of the surface of the membrane that is in contact with the electrolyte so that there are no sections of the body that are in contact with the electrolyte.

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Preferably the metal oxide is a titanium oxide.

It is preferred that the metal oxide be titania.

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According to the present invention there is also provided a method of electrochemically reducing a metal oxide in a solid state in an electrochemical cell, which electrochemical cell includes (a) a molten electrolyte, (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, (c) an anode, and (d) a membrane that separates the electrolyte and the anode and is permeable to oxygen ions and is impermeable to dissolved metal in the electrolyte, and optionally is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms, and which method includes applying a cell potential across the anode and the cathode and electrochemically reducing the metal oxide.

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Preferably, in a situation in which the metal oxide is titania, the method includes electrochemically reducing the metal oxide to titanium having an oxygen concentration of less than 0.2wt.%.

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Preferably the method includes maintaining the cell temperature below the vaporisation and/or

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decomposition temperatures of the electrolyte.

Preferably the method includes applying a cell potential above a decomposition potential of at least one constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

Preferably the membrane is formed from a solid electrolyte.

Preferably the solid electrolyte is yttria stabilised zirconia.

Preferably the metal oxide is a titanium oxide.

It is preferred that the metal oxide be titania.

In a situation in which the metal oxide is titania it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents.

In such a situation it is preferred that the method includes maintaining the cell potential above the decomposition potential for  $\text{CaO}$ .

The following example illustrates an application of the invention in the process of reducing titania into substantially pure titanium using an electrochemical cell constructed in accordance with the present invention and as illustrated schematically in Figure 1.

Whilst the example described below relates to the electrochemical reduction of titania, the basic principle is equally applicable to other metal oxides, in particular oxides of Si, Ge or alloys containing these metals.

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With reference to the figure, the electrochemical cell 2 includes a graphite-free crucible 10 made of a suitable refractory material that is essentially inert with respect to the electrolyte and electrode materials described below at cell operating temperatures.

The electrochemical cell further includes a pool 18 of molten  $\text{CaCl}_2$  electrolyte that contains at least some  $\text{CaO}$  within the crucible 10.

The electrochemical cell 2 further includes a pool 14 of molten silver or copper contained in a crucible of yttria stabilised zirconia that extends into the cell. The molten Ag or Cu forms the molten metal anode 14 of the cell. The yttria stabilised zirconia crucible 16 forms a membrane that allows migration of oxygen anions and prevents migration of calcium metal dissolved in the molten electrolyte into the molten anode. Optionally, the crucible has an outer lining of yttria.

The electrochemical cell 2 further includes a titania plate 12 positioned within a cage 24. The cage 24 (and therefore the plate 12) is suspended into the crucible 10 by means of a lead 26. This assembly forms the cathode 20 of the cell.

The electrochemical cell 2 further includes a power source 22 and electrical connections between the power source 22 and the anode 14 and the cathode 20. The connections include the above-described lead 26 and a further electrical lead 28. The electrical lead 28 is a low carbon steel wire that is consumed during the operation of the cell - as described below.

In use, power source 22 provides constant potential (voltage) settings thereby that allow the cell 2

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to draw the amount of current required during the electrolytic refining of the metal oxide body at a selected potential.

5           The electrochemical cell 2 further includes thermocouples contained in suitable heat-resistant, inert sheaths (not illustrated) for monitoring temperature in the molten metal anode 14 and the molten electrolyte 18.

10           In use, the above-described electrochemical 2 is positioned in a suitable furnace to maintain the electrolyte and the anode metal in their respective molten states. The atmosphere around the crucible 10 is preferred to be an inert gas, such as argon, that does not  
15 react with the molten electrolyte.

          Once the cell reaches its operating temperature, a preselected voltage above the decomposition potential of CaO in the electrolyte is applied to the cell, whereby  
20 reduction of the titania in the cathode is carried out as described above.

          The oxygen that passes into the electrolyte 18 by virtue of electrochemical reduction of the metal oxide is  
25 subsequently transported into the molten metal anode 14 via the membrane 16 and dissolves in the molten metal. The dissolved oxygen then oxidises the steel electrode 28, and iron oxides accumulate on the surface of the molten metal anode and are periodically removed.

30           Many modifications may be made to the preferred embodiment of the present invention described above without departing from the spirit and scope of the invention.

35           By way of example, it is noted that other shapes and configurations of the titania cathode 20 are equally

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employable, bearing in mind the need to ensure proper electric contact between the power source 22 and the titania to be reduced within the cell.

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## CLAIMS:

1. An electrochemical cell for electrochemical reduction of a metal oxide, such as titania, in a solid state, which electrolytic cell includes (a) a molten electrolyte, (b) a cathode formed at least in part from the metal oxide in contact with the electrolyte, (c) an anode, and (d) a membrane that separates the electrolyte and the anode and is permeable to oxygen cations and is impermeable to dissolved metal in the electrolyte, and optionally is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms.
2. The cell defined in claim 1 wherein the anode is a molten metal anode.
3. The cell defined in claim 1 or claim 2 wherein the anode includes a means for scavenging oxygen that is generated at the anode, in use of the cell, when oxygen anions migrate to the anode and give up electrons at the anode.
4. The cell defined in claim 2 wherein the metal of the molten metal anode has a melting point that is within the operating temperature range of the electrolyte.
5. The cell defined in claim 4 wherein the melting point of the metal of the molten metal anode is higher than the melting point of the electrolyte and lower than the vaporisation and/or decomposition temperature of the electrolyte in order to prevent electrolyte consumption and removal through vaporisation.
6. The cell defined in any one of claims 2 to 5 wherein the metal of the molten metal anode is silver or copper.



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7. The cell defined in any one of the preceding claims wherein the membrane is impermeable to the anode electrode material.
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8. The cell defined in any one of the preceding claims wherein the membrane is formed from a solid electrolyte.
- 10
9. The cell defined in claim 8 wherein the solid electrolyte is an oxide.
10. The cell defined in claim 8 wherein the solid electrolyte is yttria stabilised zirconia.
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11. The cell defined in any one of the preceding claims wherein the membrane includes a body and an outer lining, with the outer lining being in contact with the electrolyte, and the outer lining being formed from a
- 20
- material that is inert with respect to dissolved metal in the electrolyte and is impermeable to the dissolved metal.
12. The cell defined in claim 11 wherein the body is formed from the solid electrolyte.
- 25
13. The cell defined in claim 11 or claim 12 wherein the outer lining is formed from a rare earth oxide.
14. The cell defined in claim 13 wherein the rare
- 30
- earth oxide is yttria.
15. The cell defined in any one of claims 11 to 14 wherein the lining is continuous and covers all of the surface of the membrane that is in contact with the
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- electrolyte so that there are no sections of the body that are in contact with the electrolyte.

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16. The cell defined in any one of the preceding claims wherein the metal oxide is a titanium oxide.

17. The cell defined in any one of the preceding  
5 claims wherein the metal oxide is titania.

18. The cell defined in any one of the preceding claims wherein, in a situation in which the metal oxide is titania, the electrolyte is a  $\text{CaCl}_2$ -based electrolyte that  
10 includes  $\text{CaO}$  as one of the constituents.

19. A method of electrochemically reducing a metal oxide in a solid state in an electrochemical cell, which electrochemical cell includes (a) a molten electrolyte,  
15 (b) a cathode in contact with the electrolyte, the cathode being formed at least in part from the metal oxide, (c) an anode, and (d) a membrane that separates the electrolyte and the anode and is permeable to oxygen ions and is impermeable to dissolved metal in the electrolyte, and  
20 optionally is impermeable to any one or more of (i) electrolyte anions other than oxygen anions, (ii) anode metal cations, and (iii) any other ions and atoms, and which method includes applying a cell potential across the anode and the cathode and electrochemically reducing the  
25 metal oxide.

20. The method defined in claim 19 includes operating the cell with a molten metal anode.

30 21. The method defined in claim 19 or claim 20 includes maintaining the cell temperature below the vaporisation and/or decomposition temperatures of the electrolyte.

35 22. The method defined in any one of claims 19 to 21 includes applying a cell potential above a decomposition potential of at least one constituent of the electrolyte

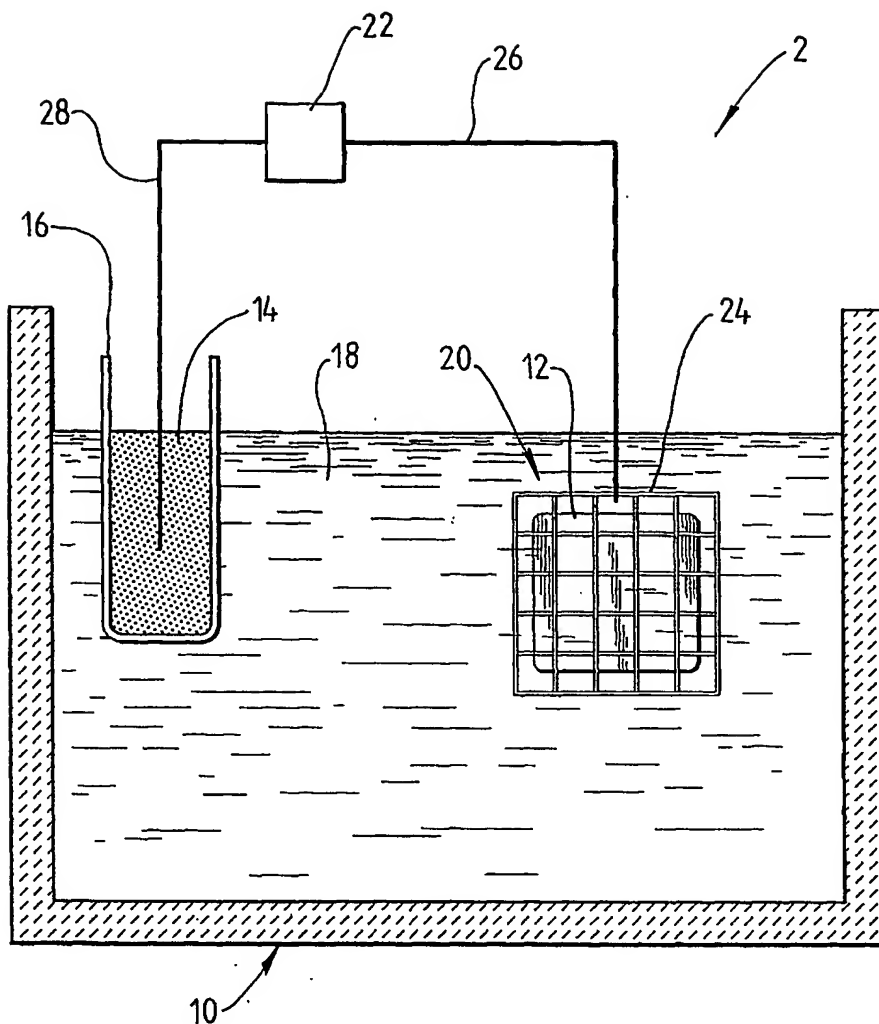
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so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

23. The method defined in any one of claims 19 to 22  
5 includes scavenging oxygen that is generated at the anode when oxygen anions migrate to the anode and give up electrons at the anode.

24. The method defined in any one of claims 19 to 22  
10 wherein, in a situation in which the metal oxide is titania, the method includes electrochemically reducing the metal oxide to titanium having an oxygen concentration of less than 0.2wt.%.

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**Fig. 1**

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